

PATENT SPECIFICATION

(11) 1434824

1434824

(21) Application No. 51899/73 (22) Filed 8 Nov. 1973
 (23) Complete Specification filed 7 Nov. 1974
 (44) Complete Specification published 5 May 1976
 (51) INT CL² C01B 31/02 31/04 C25B 11/12 H01M 4/04//4/62
 (52) Index at acceptance

C1A J210 J246 J287 J289 J370 J371 J372 J373 J385 J393
 J394 J461 J470 J476 J510 J511 J540 J5 J601 J602
 J603 J604 J606 J684 J685 J688

C7B A2C2 A9

H1B 404 462

(72) Inventors DAVID ERNEST SHIPLEY, BARRY WOODS
 WALTER FREDERICK WYSS and
 TERRY DEAN RANTELL



(54) CARBON ARTIFACTS

(71) We, COAL INDUSTRY (PATENTS) LIMITED, a company organised in accordance with the laws of Great Britain of Hobart House, Grosvenor Place, London, S.W.1. 7AE England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to carbon artifacts. In particular it relates to carbon artifacts for use as electrodes.

The invention comprises a method of manufacturing a shaped artifact for use as an electrode comprising mixing together calcined coke grist produced from a solution or extract of coal, between 1% and 40% by weight of the coke grist of carbon fibres, and a carbonisable binder at such a temperature that the binder is liquid, whereby the carbon fibres are randomly dispersed, shaping the mixture into an artifact and carbonising the binder in the shaped artifact whereby a carbon artifact is formed. Preferably less than 10% by weight of carbon fibres is employed. The invention further comprises a carbon artifact so made for use as an electrode comprising a graphite or graphitisable carbon matrix in which a calcined coke grist and between 1% and 40%, preferably less than 10%, of carbon fibres are set.

Calcined coke grist is manufactured by coking the solution or extract of coal, which is preferably liquid at the coking temperature thereof. The coke so formed is then broken up and calcined at an elevated temperature such that, and for such time that, the volatile or volatilisable matter in the coke is removed. Such temperatures are generally of the order of 1200°C to 1800°C. The calcined coke is then ground to produce the calcined coke grist.

The carbonisable binders that are generally employed comprise materials that are liquid

so that the artifact may be moulded but which can be coked or carbonised to form a material consisting essentially of carbon. In general, materials having a softening point of between 100°C and 140°C are used.

The materials generally employed as carbonisable binders are electrode binder pitches, which are usually coal tar pitches, but may be petroleum pitches or bitumens. Alternatively, solutions or extracts of coal may be employed as carbonisable binders. The amount of binder that is employed is not critical for this invention. In general, just sufficient binder should be used to enable the artifact to be shaped. A substantial excess of binder is not desirable. As a general guide, between 20% and 35% by weight of the binder may be employed, based on the weight of the shaped mixture.

The calcined coke grist may first be mixed with the carbonisable binder as above, generally about 40 deg.C above the softening point of the binder. The mixture may advantageously then be cooled, and, when solid re-ground to separate the coated and partially impregnated electrode coke grist particles. Carbon fibres, having suitable short lengths, for example 6 mm. long, are added and mixed in, in such a manner that the fibres are not seriously damaged. The mixture is then heated and extruded through a die typically at about 20 deg. C above the softening point of the binder. The extrusion or other shaping of the artifact may tend partially to align the fibres.

The carbon fibres may alternatively be added to the cokable feed stock for manufacturing the calcined coke grist so that the coke forms around the carbon fibres. If this is carried out the coke particles are reinforced by the carbon fibres. If this method is adopted it may then be necessary to add further coke grist, to which carbon fibres have not been added during the manufacture thereof, or additional carbon fibres, to the mixture.

50

55

60

65

70

75

80

85

90

As a further alternative, the carbonisable binder, the calcined coke grit and the carbon fibres are mixed together in a single operation. In this further alternative, water 5 may be added together with a small quantity of wetting agent.

Advantageously, the carbon fibres are those made from a solution or extract of coal, e.g. by methods described in British Patent 10 1,315,940. The carbon fibres may optionally have been graphitised before their incorporation into the matrix, and it is to be understood that graphitised carbon fibres are, in this specification, included in the term 15 "carbon fibres". Particularly useful materials suitable for use as the carbonisable binder are solutions or extracts of coal.

If the carbon fibres are manufactured 20 from a solution or extract of coal, it is believed that this will result in the production of an electrode which may be stronger, and have improved thermal properties. It will be understood that it is not necessarily appropriate to use the same solution or 25 extract of coal for the preparation of all three materials. However, the similarity of solutions or extracts of coal is such that their use is particularly advantageous for all three materials and may produce a stronger artifact having relatively optimised properties.

The carbonised electrode is manufactured 30 from the shaped product by heating the shaped product until the binder matrix is carbonised, for example by heating it slowly in an inert atmosphere at up to about 100°C. For the manufacture of electrodes it is generally required that the carbon should be in the form of graphite. The carbonised artifact is heated to a graphitising temperature, generally in the region of 2200°C to 40 2800°C, preferably above 2700°C, in order to convert the carbon into graphite.

The following non-limitative examples 45 illustrate the invention. The softening points of the electrode binder pitches were determined using the Ring and Ball method.

Example 1

12 g of carbon fibre, cut into 6 mm. lengths, was placed in a double sigma-bladed mixer together with 150 g electrode binder pitch (softening point 104°C) that had been ground to pass a 212 μm mesh. After 50 mixing for 30 minutes, 438 g calcined electrode coke, ground so that 50% by weight 55 passed through a 75 μm mesh, was added. Mixing was continued for a further 30 minutes at room temperature, for 30 minutes whilst the temperature was raised to 140°C and for 45 minutes at 140°C.

60 The hot mix was transferred to an extrusion press heated to 125°C. Green artifacts were extruded from a 15 mm diameter die using a driving force of 20 MN/m² on a 50 mm diameter ram.

The green artifacts were supported in a bed of calcined coke granules and baked, the temperature being increased to 200°C at 1 deg. C/min, from 200° to 550°C at 0.25 deg. C/min and from 550° to 1000°C at 1 deg. C/min.

The baked artifacts were then graphitised by being further heated to 2800°C in an inert atmosphere, which conditions were maintained for 1 h.

The artifact had a flexural strength of 28.0 MN/m². The linear coefficient of thermal expansion along the artifact was $20.4 \times 10^{-7}/\text{K}$.

An artifact was made in the same way as the previously described artifact, omitting the carbon fibre. Its flexural strength was 24.8 MN/m² and its linear coefficient of thermal expansion was $28.5 \times 10^{-7}/\text{K}$.

Example 2

12 g of carbon fibre, cut into 6 mm lengths, 88 g of electrode binder pitch (softening point 104°C) ground to pass a 212 μm mesh, and 300 g of calcined electrode coke, ground so that 50% by weight passed through a 75 μm mesh, were stirred for 60 minutes in a bowl mixer with approximately 2 imperial gallons of water and 0.5 ml of a wetting agent (for example that sold under the trade marks of Teepol or Comprox). After the mixing, as much as possible of the water was allowed to drain to waste on a filter and the cake of solids was further dried by heating at a temperature up to 40°C. The cake, i.e. the carbon fibre, the binder and the calcined coke grit, was placed in a mixer at room temperature and the mixing was continued for approximately 30 minutes while the temperature was raised to 140°C and was maintained at 140°C for 45 minutes.

The hot mix was transferred to an extrusion press heated to 125°C. Green artifacts were extruded from a 15 mm. diameter die using a driving force of 20 MN/m² on a 50 mm diameter ram.

The green artifacts were supported in a bed of calcined coke granules and baked, the temperature being increased to 200°C at 1 deg. C/min, from 200°C to 550°C at 0.25 deg. C/min and from 550° to 1000°C at 1 deg. C/min.

The baked artifacts were then graphitised by being further heated to 2800°C in an inert atmosphere, which conditions were maintained for 1 hour.

The linear coefficient of thermal expansion along the artifact was $7 \times 10^{-7}/\text{K}$. An artifact was made in the same way from the same binder and coke grit as used for the previously described artifact, omitting the carbon fibre. Its linear coefficient of thermal expansion was $17 \times 10^{-7}/\text{K}$.

All proportions in the foregoing specifi-

cation are by weight of the shaped mixture, before carbonisation.

WHAT WE CLAIM IS:—

5 1. A method of manufacturing a shaped artifact for use as an electrode, the method comprising mixing together calcined coke grist produced from a solution or extract of coal, between 1% and 40% by weight of the coke grist of carbon fibres, and a carbonisable binder at such a temperature that the binder is liquid, whereby the carbon fibres are randomly dispersed, shaping the mixture into an artifact and carbonising the binder in the shaped artifact whereby a carbon artifact is formed. 45

10 2. A method according to claim 1 in which less than 10% of carbon fibres is employed. 50

15 3. A method according to claim 1 or 2 in which the carbon fibres are produced from a solution or extract of coal. 55

20 4. A method according to any one of the preceding claims in which the carbonisable binder is a solution or extract of coal. 60

25 5. A method according to any one of claims 1 to 3 in which the carbonisable binder is an electrode binder pitch. 65

30 6. A method according to claim 5 in which the electrode binder pitch is a coal tar pitch or a petroleum pitch or a bitumen. 70

35 7. A method according to any one of the preceding claims in which between 20% and 35% by weight of the carbonisable binder is employed, based on the weight of the shaped mixture. 75

40 8. A method according to any one of the preceding claims in which the calcined coke grist and the binder are first mixed together at a first temperature above the softening point of the binder, the first mixture is cooled and, when solid, ground, the carbon fibres are subsequently mixed with the ground mixture to provide a second mixture, and the second mixture is heated and extruded at a second temperature above the softening point of the binder. 80

9. A method according to claim 8 in which the first temperature is approximately 40 deg. C above the softening point of the binder, and the second temperature is approximately 20 deg. C above the softening point of the binder. 50

10. A method according to any one of claims 1 to 7 in which the carbon fibres are first mixed with the solution or extract of coal for manufacturing the calcined coke grist, the mixture is coked whereby the coke is reinforced by the carbon fibres, and the carbonisable binder is subsequently mixed with the coke so reinforced. 55

11. A method according to any one of claims 1 to 7 in which the carbon fibres are first mixed with the carbonisable binder and subsequently the calcined coke grist is added to the mixture. 60

12. A method according to any one of claims 1 to 7 in which the carbonisable binder, the calcined coke grist and the carbon fibres are mixed simultaneously. 65

13. A method according to claim 12 in which water is added for the mixing of the carbonisable binder, the calcined coke grist and the carbon fibres. 70

14. A method according to claim 13 in which a wetting agent is added during mixing. 75

15. A method of manufacturing a shaped artifact for use as an electrode according to claim 1 substantially as hereinbefore described and with reference to Example 1 and 2. 80

16. A carbon artifact manufactured by a method as claimed in any one of the preceding claims.

For the Applicants,
J. I. WOOD,
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.